# Supporting Information

## Solvothermal synthesis of silicon hierarchical structure composed of 20 nm Si nanoparticles coated with carbon for high performance Li-ion battery anode

Jianbin Zhou,[a] Zhuoheng Jiang,[a] Wenlong Cai,[a] Xianyu Liu,[a] Yongchun Zhu,[a]* Yang Lan,[a] Kai Ma[a] and Yitai Qian[a]*

[a] Hefei National Laboratory for Physical Science at Microscale, University of Science and Technology of China, Hefei, 230026, P.R. China. Tel: +86-551-63601589; E-mail: ychzhu@ustc.edu.cn, ytqian@ustc.edu.cn.

**Experimental Section**

**Preparation of Si-20:**

Commercial $SiCl_4$, lithium foils and n-hexane are purchased from Sinopharm Chemical Reagent Co. Ltd. without further treatment. In a typical synthesis procedure, 2 ml of $SiCl_4$ solution and 6 ml of n-hexane were homogeneous mixed by stirring. And then, the mixture and 0.48 g of lithium foils were transported into a stainless steel autoclave (volume 20 mL). The above steps were conducted in a glove-box filled with Ar. And then, the autoclave was annealed at 280 ˚C for 10 h with a heating rate of 5 ºC/min. After that, the autoclave was cooled down to room temperature naturally and the collected products were washed with diluted HCl solution and then washed with deionized water 3 times and ethanol 1 time. Finally, the products were dried in vacuum oven at 60 ºC overnight. Then, silicon hierarchical structure composed of 20 nm Si nanoparticles can be obtained.

**Preparation of Si-20@C:**

The above obtained Samples were loaded into tube furnace at 600 ºC for 4 h with controlled $C_2H_2$ ($C_2H_2$: 10 % and Ar: 90 %) airflow speed of 8 ml/min. The heating ramp rate was 10 °C/min. After cooling down, Si-20@C can be obtained.

**Material characterization:**

The phases of samples were collected on X-ray diffraction ( XRD, Philips, X'pert X-ray diffractometer with Cu *K*a, λ=1.54182 Å). The morphology of samples were examined by Scanning electron microscopy (SEM, JEOL-JSM-6700F), transmission electron microscopy (TEM, Hitachi H7650) and High resolution transmission electron microscopy (HRTEM, JEM-ARM 200F). The composition of products were confirmed by Raman spectroscopy (Lab-RAM HR UV/VIS/NIR), X-ray fluorescence (XRF, XRF-1800), and energy dispersive x-ray spectroscopy (EDX, JEM-ARM 200F).

**Electrochemical characterization:**

The electrochemical properties of the samples were tested in half cells (2016 R-type). To prepare electrodes, the active materials, acetylene black and carboxymethylcellulose sodium with a weight ratio of 60: 20: 20 were homogeneously mixed with water. The slurry was coated on a copper foil

and dried at 80 ˚C for 10 h in a vacuum oven. The mass of the active materials was measured to be 1-2 mg/cm$^2$. To assemble the half cells, lithium foil was used as the counter electrode, Celgard 2400 and a solution of 1 M $LiPF_6$ in a mixture of ethylene carbonate/dimethylcarbonate (EC/DMC; 1:1 by Volume) and 5 wt% fluoroethylene carbonate (FEC) was used as the separator and the electrolyte respectively, respectively. Cyclic voltammogram (CV) was conducted on electrochemical workstation (CHI660D) in the voltage window of 0.01-1.5 V with a scanning rate of 0.1 mV/s. test The rate performance and cycling properties of simple were collected on a battery tester (LANDCT2001A) at different current densities. The electrochemical impedance spectroscopy (EIS) was conducted on a CHI660D electrochemical workstation with an alternating current (AC) voltage of 0.005 V in the frequency range from 100 KHz to 0.1 Hz.

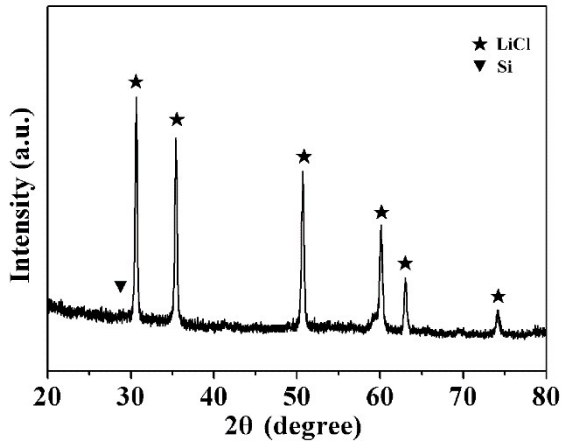


Fig. S1 XRD pattern of crude products after reaction without further treatment.

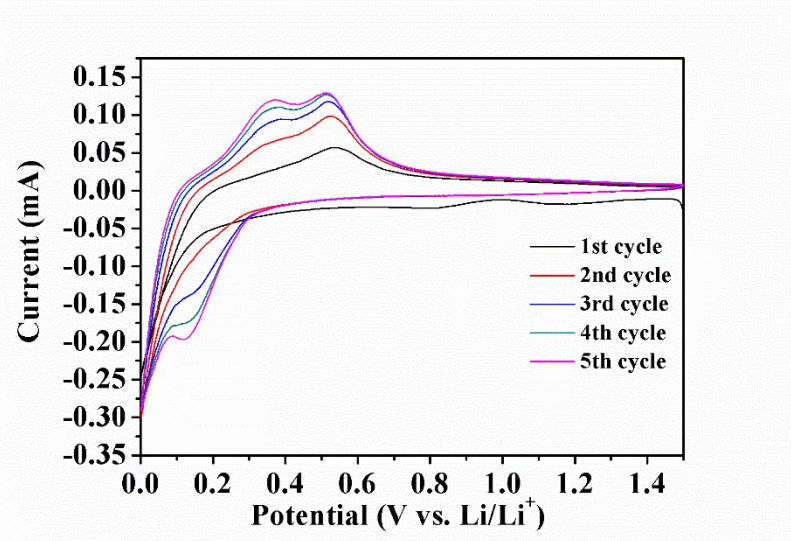


Fig. S2 CV curves of Si-20@C in the first five cycles.

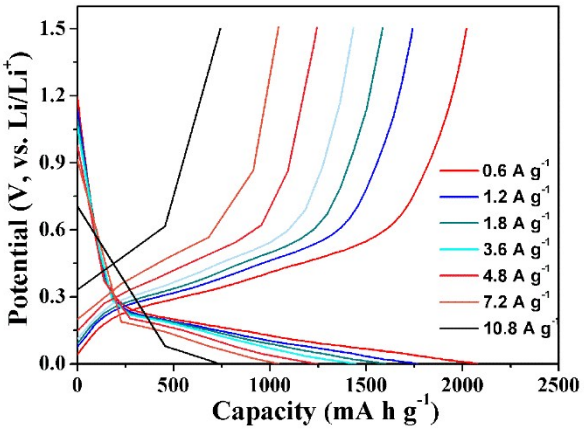


Fig. S3 The discharge-charge potential curves of Si-20@C at the current densities of 0.6, 1.2, 1.8, 3.6, 4.8, 7.2 and 10.8 A $g^{-1}$.

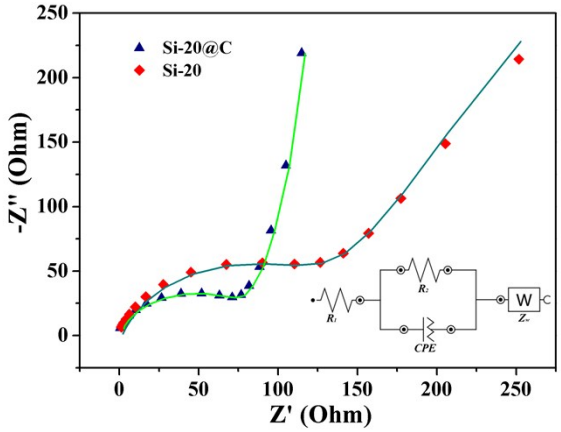


Fig. S4 The Nyquist plots of Si-20 and Si-20@C (Dotted lines are experimental data and the solid lines are the fitting data). Equivalent circuits used to fit the testing data (the inset).

Fig. S4 shows the EIS of Si-20 and Si-20@C. The semicircle at high-to-medium frequency reflects interfacial charge transfer process and and the slope line at low frequency reflects Warburg diffusion impedance. After fitting by an equivalent circuit as shown in Fig. S4, the detailed information are listed in Table S1. The low resistance of the electrolyte ($R_1$) and charge transfer resistance ($R_2$) of Si-20 indicate the advantages of Si nanostructure. The decreased $R_1$ and $R_2$ of Si-20@C reveal the contribution of coated carbon layer.

Table S1 Equivalent-circuit parameters obtained from fitting the experimental impedance spectra

| Sample | $R_1(\Omega)$ | $R_2(\Omega)$ |
|---|---|---|
| Si-20 | 0.27 | 96 |
| Si-20@C | 0.13 | 61 |